



## DECLARATION

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I, Hajime Inoue, a Patent Attorney, of Ogikubo TM Bldg. 2F, 5-26-13, Ogikubo, Suginami-ku, Tokyo 167-0051, Japan, solemnly and sincerely declare:

that I have a thorough knowledge of Japanese and English languages; and

that the attached pages contain a correct translation into English of the specification of the following Japanese Patent Application:

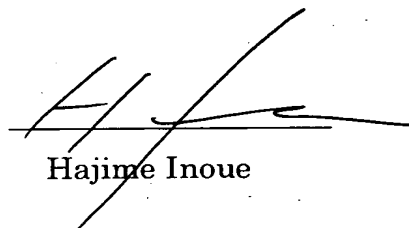
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Hajime Inoue

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H01M 10/36

[Title of the Invention] ELECTRODE MATERIAL FOR LITHIUM SECONDARY BATTERY AND LITHIUM SECONDARY BATTERY USING THE SAME

[Number of Claims] 11

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[Official Fee for Filing]

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[Amount] 21000

[List of the Documents Attached]

[Document]	Specification	1 copy
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[Document]	Drawings	1 copy
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[Document]	Abstract	1 copy
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[DOCUMENT NAME] SPECIFICATION

[TITLE OF THE INVENTION] ELECTRODE MATERIAL FOR LITHIUM  
SECONDARY BATTERY AND LITHIUM SECONDARY BATTERY USING THE  
SAME

5 [CLAIMS]

[Claim 1] An electrode material for a lithium secondary battery,  
comprising a carbon fiber formed with vapor growth, the carbon fiber having a number  
of bottomless cup-shaped carbon mesh layers stacked together,

10 wherein an area of a portion of the edges of the carbon mesh layers exposed on  
the exterior surface of the carbon fiber is equal to or larger than 2% of an area of the  
exterior surface of the carbon fiber.

[Claim 2] The electrode material for a lithium secondary battery as  
defined in claim 1,

15 wherein the carbon fiber is of a hollow structure with no bridge and has a  
length of several tens of nanometers.

[Claim 3] The electrode material for a lithium secondary battery as  
defined in claim 1 or 2,

20 wherein an area of a portion of the edges of the carbon mesh layers exposed on  
the surface of the carbon fiber is equal to or larger than 7% of an area of the surface of  
the carbon fiber.

[Claim 4] The electrode material for a lithium secondary battery as  
defined in claim 1, 2, or 3,

25 wherein the surface portion of the carbon fiber on which the edges of the  
carbon mesh layers are exposed is irregular and has minute irregularities at the level of  
atomic size.

[Claim 5] The electrode material for a lithium secondary battery as  
defined in claim 1, 2, 3, or 4,

wherein the number of stacked carbon mesh layers are in a range between several tens of thousands and several hundreds of thousands.

[Claim 6] The electrode material for a lithium secondary battery as defined in claim 1, 2, 3, 4, or 5,

5 wherein the inner edges of the carbon mesh layers are exposed.

[Claim 7] The electrode material for a lithium secondary battery as defined in any one of claims 1 to 6,

wherein an electrolyte introduced and held in the hollow portion of the carbon fiber.

10 [Claim 8] The electrode material for a lithium secondary battery as defined in any one of claims 1 to 7,

wherein the carbon fiber is an anode material.

[Claim 9] The electrode material for a lithium secondary battery as defined in any one of claims 1 to 7,

15 wherein the carbon fiber is a cathode material.

[Claim 10] A lithium secondary battery in which the anode material as defined in claim 8 is used for an anode.

[Claim 11] A lithium secondary battery in which the cathode material as defined in claim 9 is used for a cathode.

20 [DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[TECHNICAL FIELD OF THE INVENTION]

The present invention relates to an electrode material for a lithium secondary battery and a lithium secondary battery using the same.

25 [0002]

[PRIOR ART]

Among various types of secondary batteries, a lithium secondary battery is

used as a power supply indispensable for information communications equipment represented by portable telephones and notebook personal computers, and contributes to reduction of the size and weight of mobile equipment.

Graphite or carbon fibers are used as an electrode material (additive) for such a lithium secondary battery in order to attain various purposes such as increase of the strength, application of the electrical conductivity and the like.

Both the cathode and anode materials in the lithium secondary battery are of layered structure. Upon charging, lithium ions are extracted from the cathode and introduced between the carbon mesh layers of the anode to form a lithium intercalation compound. Upon discharging, reversely, a reaction occurs in which lithium ions moves from the carbon anode to the cathode.

As described above, the carbon electrode material has a function of occluding and releasing lithium ions. The quality of this occluding and releasing function greatly influences the battery characteristics such as charging and discharging.

[0003]

#### [PROBLEM TO BE SOLVED BY THE INVENTION]

Graphite and particularly anisotropic graphite has a typical layered structure in which graphite intercalation compounds (GICs) are formed by introducing various types of atoms and molecules. When lithium ions are introduced between the graphite layers, the electrode materials (and particularly the anode material) are expanded due to increase of the gaps between the layers. If the charging and discharging are repeated in such a state, the electrode may be deformed or lithium metal may easily be separated out. This leads to capacity deterioration or internal short-circuiting. Moreover, if the gaps between the layers are repeatedly expanded and contracted, the crystal graphite structure will be broken, whereby the cycle characteristic (lifetime) of the battery may be adversely affected. In addition, there is a problem in that the graphite is inferior to the electrical conductivity as the electrode material.

On the other hand, it is also known that the carbon materials may include a tubular carbon fiber produced with vapor growth. This carbon fiber is of a tubular configuration which is consisted of a plurality of concentrically arranged carbon mesh layers. When it is to be used as anode material, it raises another problem in that the lithium ions can be introduced only into the edge of the fiber, thereby forming lithium intercalation compounds insufficient to provide a satisfactory electric energy density and thus capacity. Moreover, the concentrically arranged carbon mesh layers raise a further problem in that when the lithium ions are introduced, these layers will forcedly be expanded to create a stress, also resulting in breaking of the crystal structure.

Moreover, there is raised a further problem in that the electrode reinforcing effect is insufficiently provided since the tubular carbon fiber does not have a degree of freedom relating to its shape flexibility, thereby being weaker against stresses such as buckling, tensioning, twisting and the like.

[0004]

The present invention is thus made in view of the above-mentioned problem and its object is to provide an electrode material for a lithium secondary battery which can provide an increased lifetime, electric energy density and capacity and which is superior in electrical conductivity and electrode reinforcement, and a lithium secondary battery using such an electrode material.

[0005]

[MEANS TO SOLVE THE PROBLEMS]

An electrode material for a lithium secondary battery according to the present invention is characterized by that it comprises a carbon fiber formed with vapor growth, the carbon fiber having a number of bottomless cup-shaped carbon mesh layers stacked together, and an area of a portion of the edges of the carbon mesh layers exposed on the exterior surface of the carbon fiber is equal to or larger than 2% of an area of the exterior surface of the carbon fiber.

The carbon fiber is characterized by that it is of a hollow configuration with no bridge along its length of several tens of nanometers.

Furthermore, it is preferable that an area of a portion of the edges of the carbon mesh layers exposed on the surface of the carbon fiber is equal to or larger than 7% of an area of the surface of the carbon fiber.

Moreover, the carbon fiber of the present invention is characterized by that the surface portion thereof on which the edges of the carbon mesh layers are exposed is irregular and has minute irregularities in the level of atomic size.

Furthermore, the carbon fiber of the present invention is characterized by that the stacked carbon mesh layers are in a range between several tens of thousands and several hundreds of thousands.

Moreover, the carbon fiber of the present invention is characterized by that the inner edges of the carbon mesh layers are exposed.

Furthermore, an electrolyte can be introduced and held in the hollow portion of the carbon fiber.

The carbon fiber can be used as a cathode material in the lithium secondary battery (electrode additive) and also as an anode material (main electrode material or additive).

In addition, the lithium secondary battery according to the present invention is characterized by that the electrode material is used in the cathode and/or anode.

[0006]

#### [EMBODIMENTS OF THE INVENTION]

Several preferred embodiments of the present invention will now be described in detail with reference to the attached drawings.

First of all, an electrode material will be described.

In this embodiment, as the aforementioned electrode material, a carbon fiber formed with vapor growth (which will be referred to "carbon fiber of herring-bone



structure") is used in which a great number (several tens of thousands to several hundreds of thousands) of bottomless cup-shaped carbon mesh layers stacked together and in which an area of a portion of the edges of the carbon mesh layers exposed on the exterior surface of the carbon fiber is equal to or more than 2% of an area of the surface of the carbon fiber.

The carbon fiber is of hollow configuration which does not have internal bridges over its length of several tens of nanometers.

The carbon fiber of herring-bone structure is known in the art, but an example of vapor growth processes will be described below.

A reactor used was a known vertical reactor.

Benzene was used for a raw material and fed into a reactor chamber with the flow of hydrogen in a flow rate of 0.31/h under a partial pressure equal to the vapor pressure at about 20 degrees Celsius. A catalyst used was ferrocene which was vaporized at 185 degrees Celsius and fed into the chamber at a density of about  $3 \times 10^{-7}$  mol/s. The reaction temperature was about 1100 degrees Celsius while the reaction time was about 20 minutes. Thus, a carbon fiber of herring-bone structure having its average diameter of about 100nm was obtained. In addition, the raw material, catalyst, reaction conditions are not limited to those of the above-mentioned example. By changing the reaction conditions, there can be provided various carbon fibers having different diameter and length.

[0007]

FIG. 1 is a copy of a transmission electron microscope photograph of a carbon fiber of herring-bone structure produced according to the aforementioned vapor growth process; FIG. 2 is an enlarged view of FIG. 1; and FIG. 3 is a diagrammatic view of FIG.

1.

As will be apparent from these figures, the carbon fiber has a structure that a number of bottomless cup-shaped carbon mesh layers 10 are stacked together. The

exterior surface of the carbon fiber includes an amorphous deposited layer 12 of excess carbon formed thereon. The thickness of the deposited layer 12 is equal to about several nanometers. Reference numeral 14 denotes a center hole. This center hole has a sufficient space to hold an electrolyte. As will be apparent from FIGs. 1 to 3, the carbon fiber comprises a number of bottomless cup-shaped carbon mesh surfaces 10 stacked together and is of hollow configuration extending over several tens of nanometers without bridge.

When the carbon fiber formed with such a deposited layer 12 is heated in the atmosphere for one or several hours at a temperature equal to or higher than 400 degrees Celsius and preferably equal to or higher than 500 degrees Celsius and more preferably between 520 degrees Celsius and 530 degrees Celsius, the deposited layer 12 is oxidized and pyrolyzed. As a result, the deposited layer 12 is removed to partially expose the edges of the carbon mesh layers (or six-membered ring edges).

Alternatively, the deposited layer 12 may be removed to expose the edges of the carbon mesh layers by washing the carbon fiber with supercritical water.

Furthermore, the deposited layer 12 can be removed even by dipping the aforementioned carbon fiber into hydrochloric acid or sulfuric acid and heating it up to about 80 degrees Celsius while stirring using a stirrer.

[0008]

FIG. 4 is a copy of a transmission electron microscope photograph of a carbon fiber of herring-bone structure which has been heat-treated in the atmosphere for one hour at a temperature of about 530 degrees Celsius as described; FIG. 5 is an enlarged view of FIG. 4; FIG. 6 is a diagrammatic view of FIG 5.

It is apparent from FIGs. 4 to 6 that such a heat-treatment partially removes the deposited layer 12 to expose the edges of the carbon mesh layers 10 (or carbon six-membered ring edges). It is, however, believed that the remaining parts of the deposited layer 12 are also almost pyrolyzed and thus simply in contact with the carbon

fiber. If the heat-treatment is further performed for several hours while at the same time the carbon fiber is washed with supercritical water, 100% of the deposited layer 12 can be removed.

The inner edges of the carbon mesh layers 10 are also exposed.

5 [0009]

The edge of each of the exposed carbon mesh layer 10 is easy to bond other atoms and thus extremely active. Moreover, the carbon fiber includes irregularities 16 for providing a great anchoring effect.

10 Actually, it has been found that when an anode was formed by bonding a number of such carbon fibers together through a resin binder, applying the bonded carbon fibers on a copper foil and then drying such an assembly, a good bonding force to the binder was provided, resulting in prolongation of the lifetime thereof.

As can be seen from FIGs. 5 and 6, the portions of the outer and inner surfaces on which the edges of the carbon mesh layers 10 are exposed show irregular edges and exhibit the irregularities 16 in the level of nanometer or atomic size. These irregularities 16 was exposed by removing the deposited layer 12 through the aforementioned heat-treatment, although it was not clearly seen before removal of the deposited layer 12 as shown in FIG. 2. Thus, the irregularities create an anchoring effect that more strongly bond the carbon fibers to the binder.

20 [0010]

FIG. 7 shows Raman spectra in a carbon fiber having a herring-bone structure (sample No. 24PS) after it has been heat-treated in the atmosphere for one hour at temperatures of 500 degrees Celsius, 520 degrees Celsius, 530 degrees Celsius and 540 degrees Celsius, respectively.

25 Although the removal of the deposited layer 12 through the aforementioned heat-treatment has been described in connection with FIGs. 4 to 6, the Raman spectra of FIG. 7 clearly show the fact that this sample is a carbon fiber and also has no

graphitized structure, from the presence of D peak ( $1360\text{cm}^{-1}$ ) and G peak ( $1580\text{cm}^{-1}$ ).

[0011]

In other words, it is believed that the aforementioned carbon fiber of herring-bone structure has a turbostratic structure in which the carbon mesh faces are shifted (or ground).

This carbon fiber of turbostratic structure has a stacked structure in which the hexagonal carbon mesh layers are arranged parallel to one another, but such a stacked structure includes hexagonal mesh layers shifted or rotated in the horizontal direction and does not have any crystallographic regularity.

The feature of this turbostratic structure is that the intercalation between the layers is hard to occur. However, atoms in the level of such a size as in lithium ion are permitted to intercalate between the layers.

[0012]

FIG. 8 shows Raman spectra of carbon fibers, samples No. 19PS and No. 24PS, which caused the edges of carbon mesh layers to be exposed through the aforementioned heat-treatment.

FIG. 9 shows Raman spectra of the same carbon fiber samples No.19PS and No.24PS which have been heat-treated at 3000 degrees Celsius (normal graphitization process) after the edges of the aforementioned carbon mesh layers had been exposed.

It can be seen from FIG. 9 that the D peaks remain even if the graphitization is performed for the carbon fibers in which the edges of the carbon mesh layers are exposed. This means that the carbon fiber is not graphitized by the graphitization.

A diffraction line did not appear at the 112 plane in X-ray diffractometry (not shown). This also shows that the carbon fiber was not graphitized.

[0013]

It is conceivable that the carbon fiber is not graphitized by the graphitization since the deposited layer 12 which can easily be graphitized has been removed. It has

also found that the remaining parts of the herring-bone structure are not graphitized.

The carbon fiber thus obtained in which the edges of the carbon mesh layers are exposed can be used as an electrode material for a lithium secondary battery (or electrode additive).

5 [0014]

The electrode material (carbon fiber) of this embodiment is extensible in the longitudinal direction, since a great number of bottomless cup-shaped carbon mesh surfaces 10 are stacked to provide a hollow structure having no bridge along the length of several tens of nanometers thereof. When the lithium ions enter between the carbon mesh layers through the outer and inner surfaces, the gaps between the carbon mesh layers are expanded to elongate the carbon fiber in the longitudinal direction (FIG. 10). On the contrary, when the lithium ions are released from between the gaps between the carbon mesh layers 10, these gaps are reduced to shorten the carbon fiber in the longitudinal direction (FIG. 11).

15 This means that in fact, the carbon fiber will not substantially be subjected to physical stress without breaking its crystal structure since any stress created due to the repeated entering and releasing of the lithium ions is absorbed by the expansion and contraction of the carbon fiber and also since the entering and releasing of the lithium ions are performed through both the outer and inner surfaces of the carbon fiber. This also improves the high power and lifetime properties in the battery with the performance being stabilized.

[0015]

25 In this regard, if the graphite is used as anode material, its crystal structure is easily be broken since graphite is hard to be simply expanded and recovered through the entering and releasing of the lithium ions. If a tubular carbon fiber consisting of concentrically stacked carbon mesh layers is used as anode material, a great stress will be repeatedly exerted to the carbon fiber since the lithium ions penetrate through the

edge of the tube forcibly.

[0016]

The electrode material (carbon fiber) in this embodiment has such a feature that the edges of the bottomless cup-shaped carbon mesh layers exposed through the inside and outside of the fiber have an extremely high activity. The lithium ions may easily be adsorbed onto the edges having such a high activity. Therefore, a larger occlusion for lithium ions may be provided. This leads to the fact that the battery capacity can be increased. In addition, the fact that the electrolyte is also held in the center hole 14 of the carbon fiber assists the occlusion of more lithium ions at the edges exposed within the fiber and leads to increase of the battery capacity.

[0017]

The anode is formed by applying and hardening the binder-bonded electrode material onto an electrode foil such as copper foil or the like. The binder used may include various resins such as epoxy resin, Teflon (trade name) resin and the like. The content of the binder may be about 5 wt%. For the anode, the graphite may be used as chief material and contain the aforementioned electrode material as additive.

The cathode is formed by applying and hardening the aforementioned electrode material and lithium containing oxides bonded together by the binder on an electrode foil such as aluminum foil or the like. The lithium containing oxides may include various oxides such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$  and the like.

If the aforementioned carbon fiber is used as electrode additive, one or more wt% of the carbon fiber may be added into the electrode.

[0018]

The electrolyte may be any known liquid or gelled electrolytes such as a liquid electrolyte using propylene carbonate as a solvent and lithium perchlorate as a solute or a gelled polymer created by adding a small quantity of organic polymer into such a liquid electrolyte.

The lithium secondary battery can be formed by attaching leads to the anode and cathode, winding the anode and cathode through an insulation separator of porous membrane, placing such an assembly in a casing and sealing the casing after the electrolyte has been impregnated.

5           FIG. 12 shows a button-shaped lithium secondary battery.

In this figure, reference numeral 21 denotes an upper lid; 22 cathode; 23 a glass filter; 24 anode (anode materials +PTFE); 25 a packing; 26 a lower lid; and 27 an electrolyte.

FIG. 13 shows a polymer type lithium secondary battery.

10           In this figure, reference numeral 28 designates an electrode film; 29 an anode; 30 a polyelectrolyte; and 32 an electrode film.

[0019]

As discussed above, the electrode material according to this embodiment comprises a carbon fiber formed by stacking a number of bottomless cup-shaped  
15 carbon mesh layers 10 to provide a hollow structure having no bridge over the length of several tens of nanometers thereof. Thus, it has an increased flexibility in comparison with a simply tubular carbon fiber. The electrode material of the present invention is stronger against various stresses such as buckling, tensioning, twisting and the like and has a superior electrode reinforcing effect and a superior electrical conductivity.

20           In particular, the anode formed of the aforementioned electrode material has superior occlusion and release properties for lithium ions and an increased energy density which can highly increase the battery capacity. Moreover, this carbon fiber has an improved stretchability. Thus, it can expand and contract depending on the entering and releasing of lithium ions to absorb the stresses. Even if the charging and discharging  
25 are repeatedly performed, the crystal structure of the carbon fiber will not be broken, resulting in improvement of the battery lifetime.

[0020]

## [ADVANTAGES OF THE INVENTION]

As above described, the present invention can provide an electrode material for a lithium secondary battery which can provide a high power, an increased lifetime, a stabilized performance and an increased battery capacity and which is superior in electrical conductivity and electrode reinforcement, and a lithium secondary battery using such an electrode material.

## [BRIEF DESCRIPTION OF THE DRAWINGS]

### [FIG. 1]

FIG. 1 is a copy of a transmission electron microscope photograph of a carbon fiber of herring-bone structure produced according to the aforementioned vapor growth process.

### [FIG. 2]

FIG. 2 is an enlarged view of FIG. 1.

### [FIG. 3]

FIG. 3 is a diagrammatic view of FIG. 2.

### [FIG. 4]

FIG. 4 is a copy of a transmission electron microscope photograph of a carbon fiber of herring-bone structure which has been heat-treated in the atmosphere for one hour at a temperature of about 530 degrees Celsius.

### [FIG. 5]

FIG. 5 is an enlarged view of FIG. 4.

### [FIG. 6]

FIG. 6 is a diagrammatic view of FIG. 5.

### [FIG. 7]

FIG. 7 shows Raman spectra in a carbon fiber having a herring-bone structure (sample No. 24PS) after it has been heat-treated in the atmosphere for one hour at temperatures of 500 degrees Celsius, 520 degrees Celsius, 530 degrees Celsius and 540



degrees Celsius, respectively.

[FIG. 8]

FIG. 8 shows Raman spectra of carbon fibers, samples No. 19PS and No. 24PS, which caused the edges of carbon mesh layers exposed through the aforementioned heat-treatment.

[FIG. 9]

FIG. 9 shows Raman spectra of the same carbon fiber samples No. 19PS and No. 24PS heat-treated at 3000 degrees Celsius (normal graphitization process) after the edges of the aforementioned carbon mesh layers have been exposed.

[FIG. 10]

FIG. 10 illustrates lithium ions entered between the carbon mesh layers.

[FIG. 11]

FIG. 11 illustrates lithium ions released from between the carbon mesh layers.

[FIG. 12]

FIG. 12 shows a button-shaped lithium secondary battery.

[FIG. 13]

FIG. 13 shows a polymer type lithium secondary battery.

[EXPLANATION OF REFERENCE NUMERALS]

CARBON MESH LAYERS

DEPOSITED LAYER

CENTER HOLE

IRREGULARITIES

UPPER LID

CATHODE

GLASS FILTERS

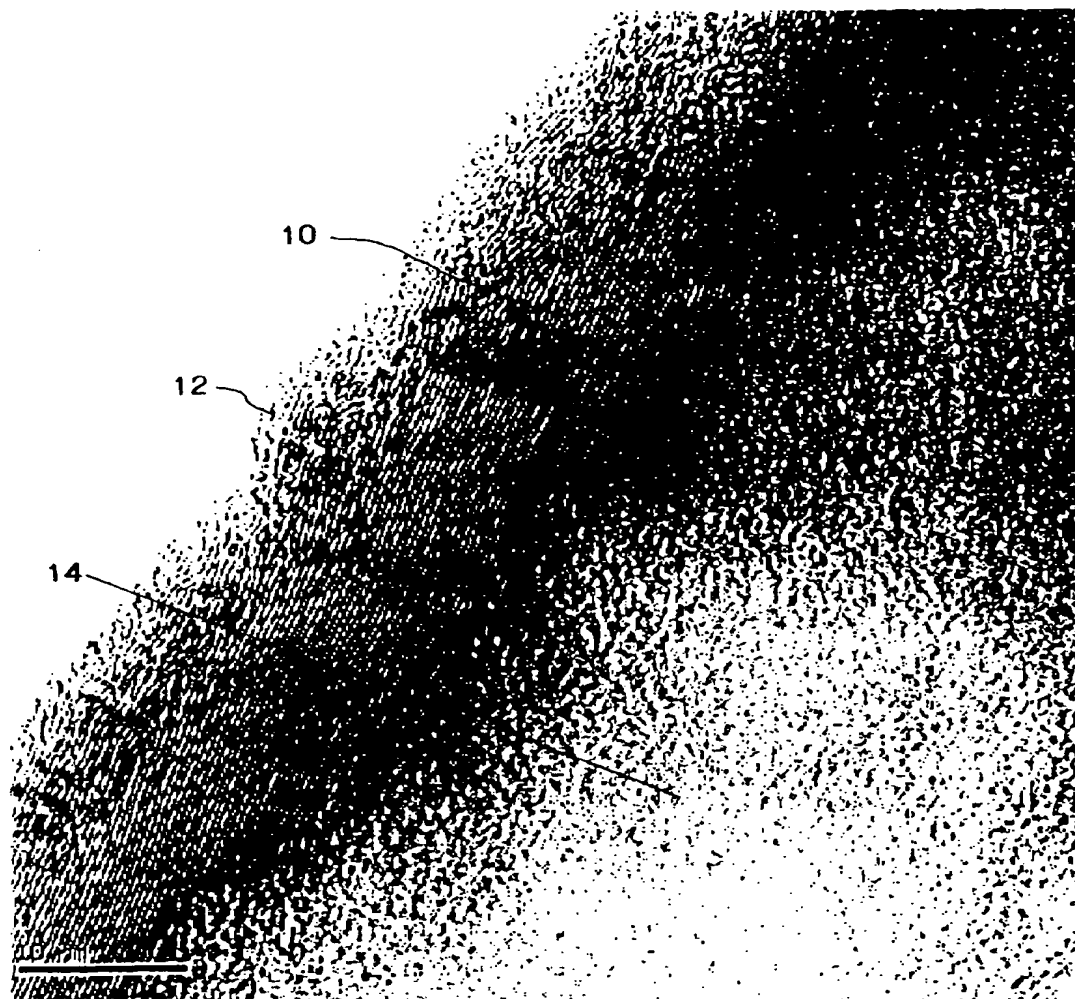
ANODE

PACKING

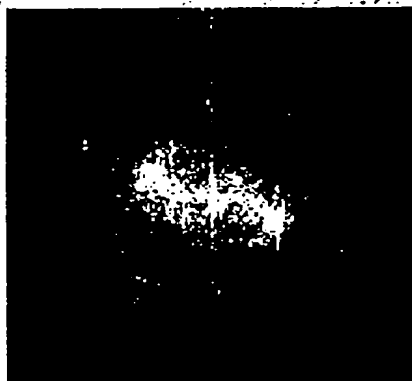
	26	LOWER LID
	27	ELECTROLYTE
	28	ELECTRODE FILM
	29	ANODE
5	30	POLYELECTROLYTE
	32	ELECTRODE FILM

[Title of the Document] Drawings

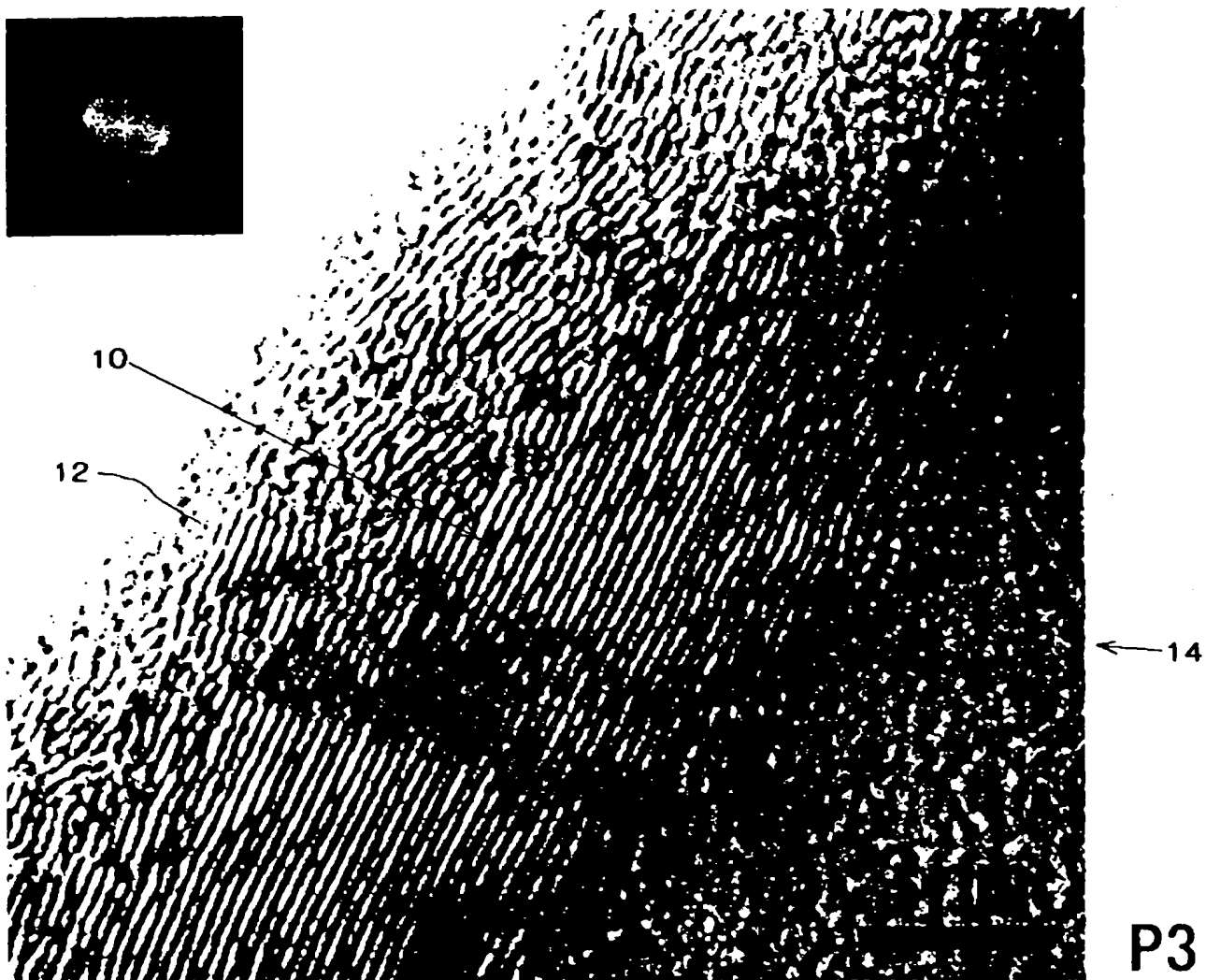
**FIG. 1**



p3



**FIG. 2**



**FIG. 3**

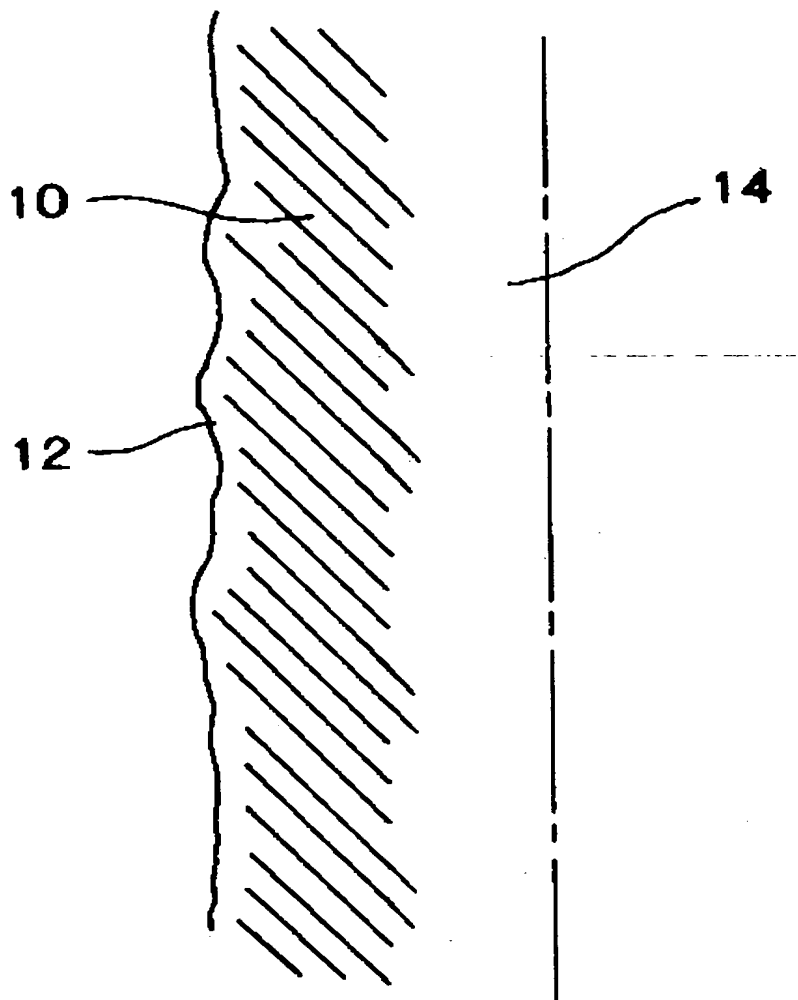
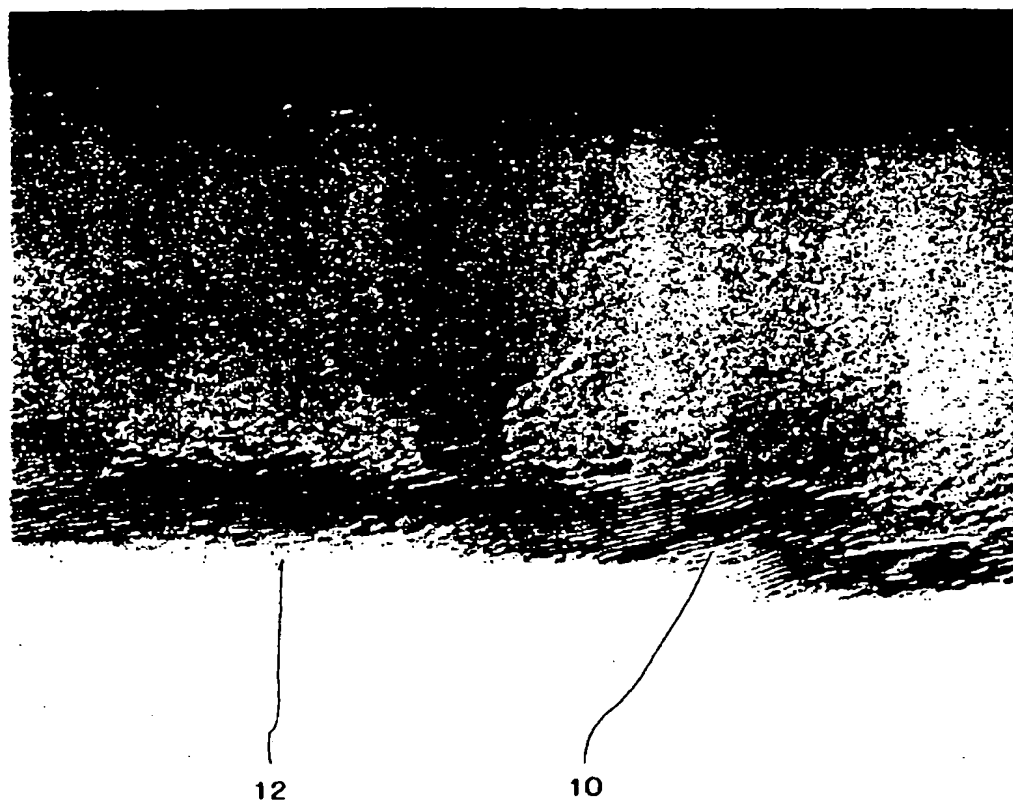


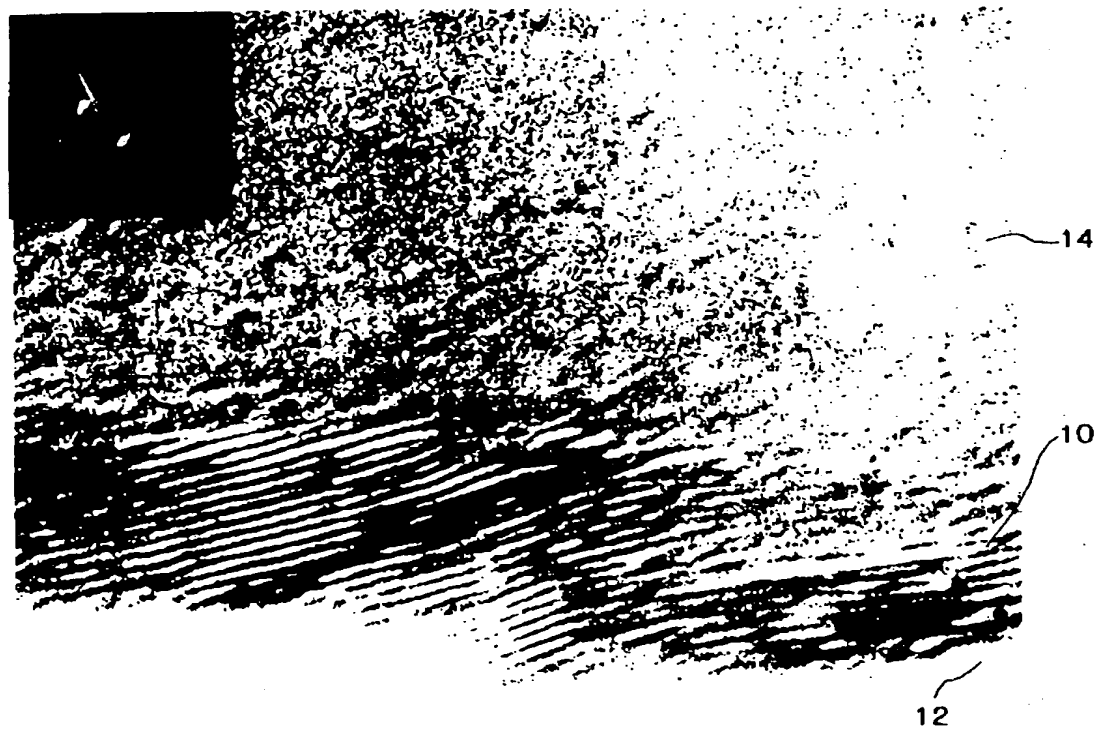
FIG. 4



P3 ox



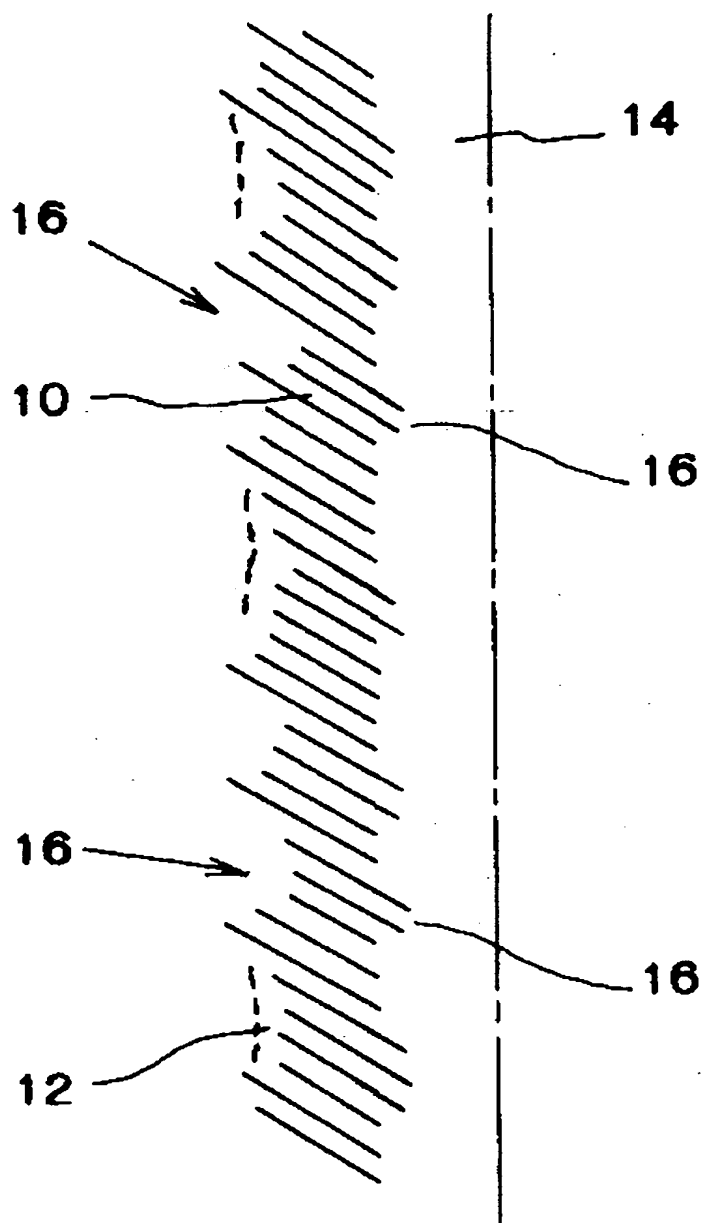
FIG. 5



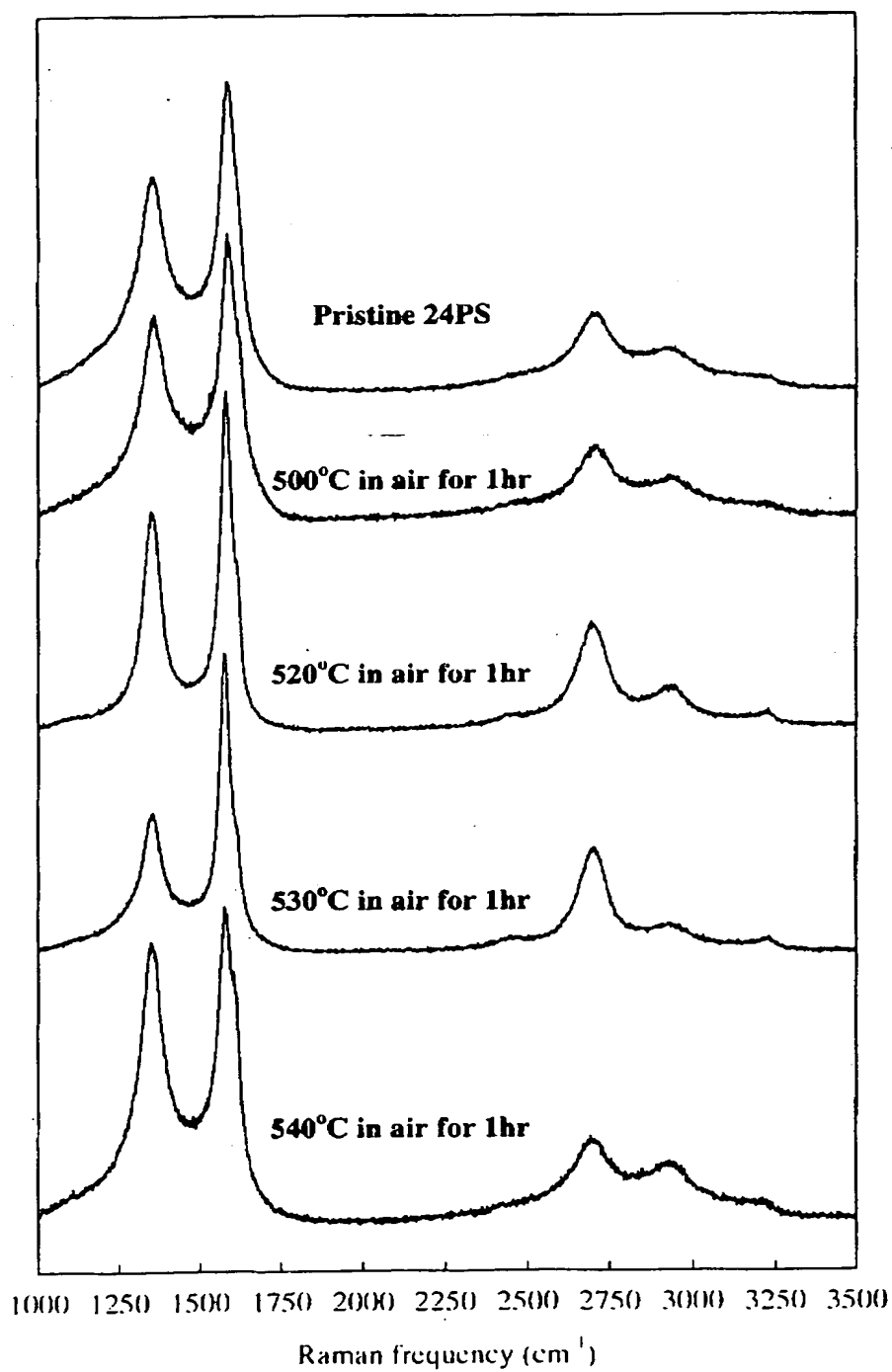
**3nm**

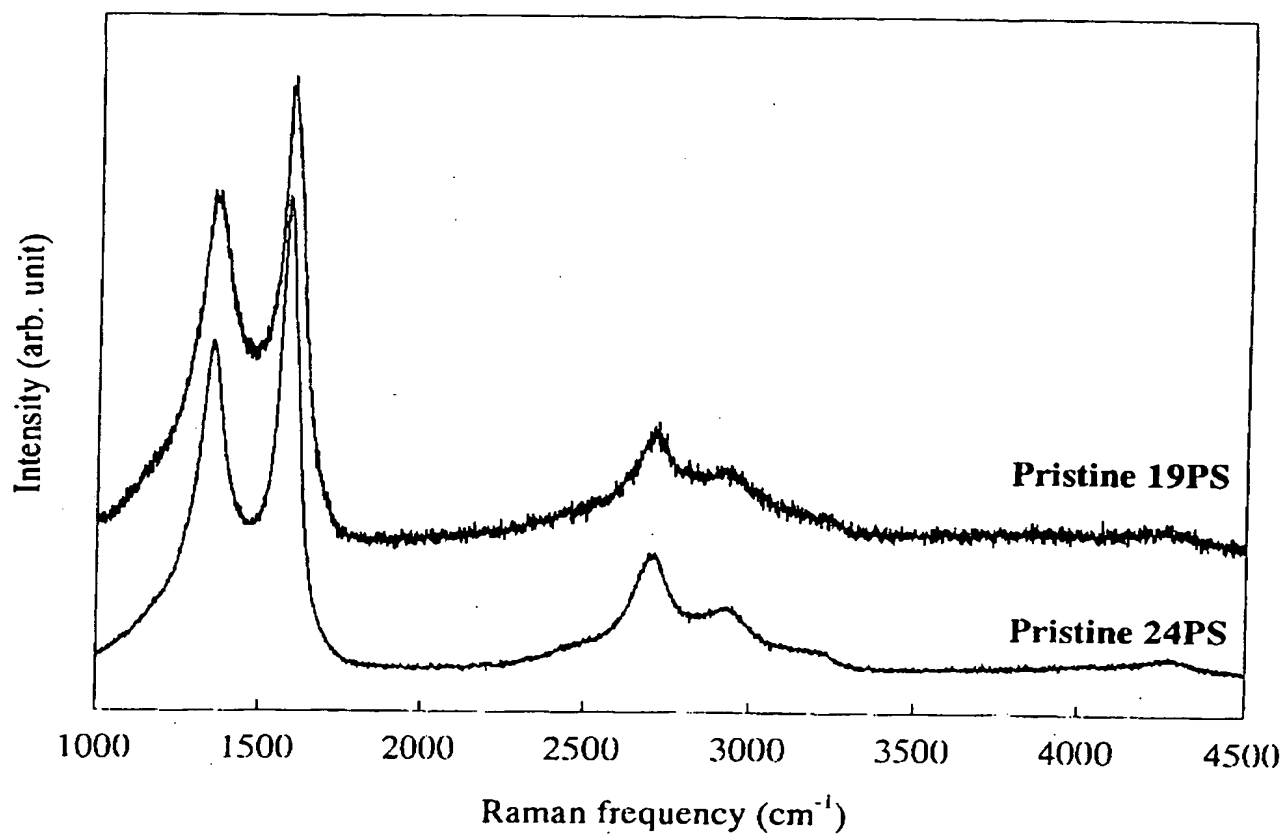
P3 oxy

FIG. 6





**FIG. 7**

**FIG. 8**

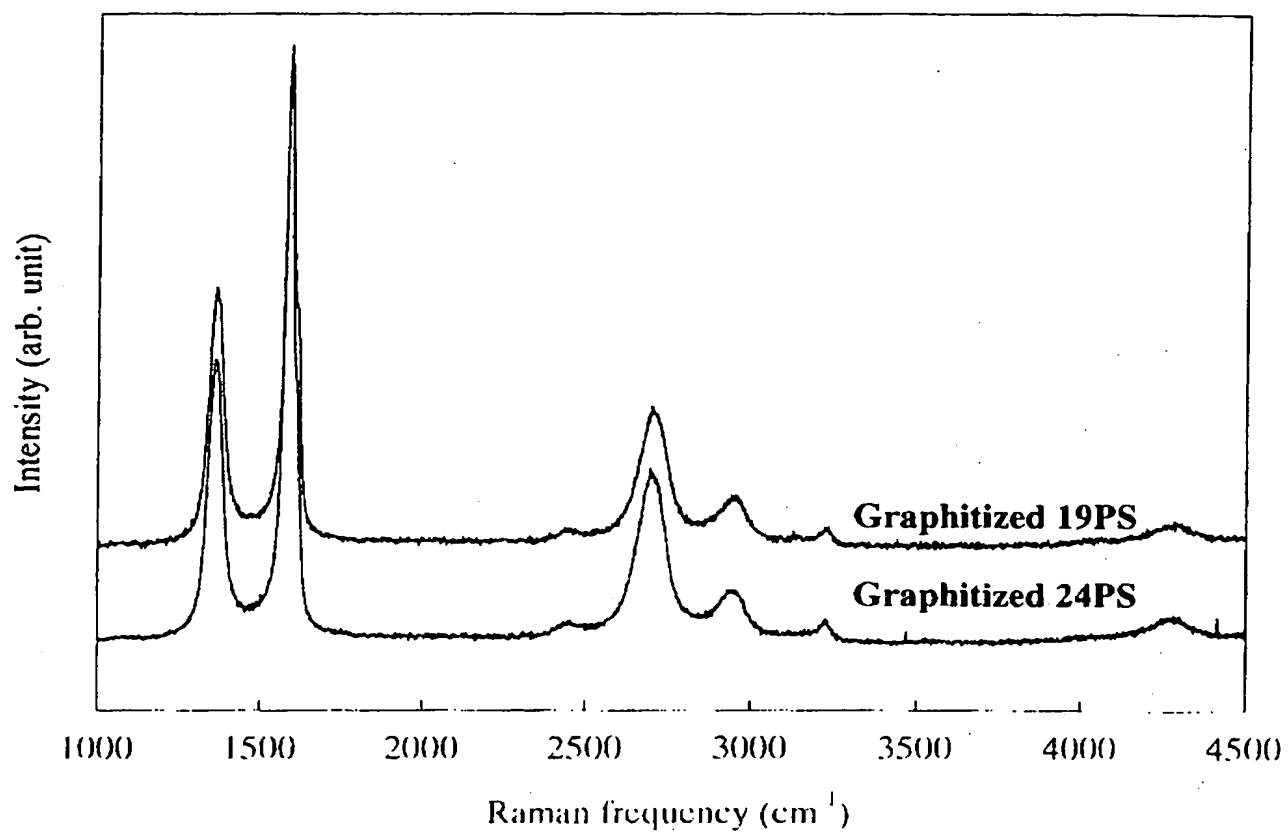
**FIG. 9**

FIG. 10

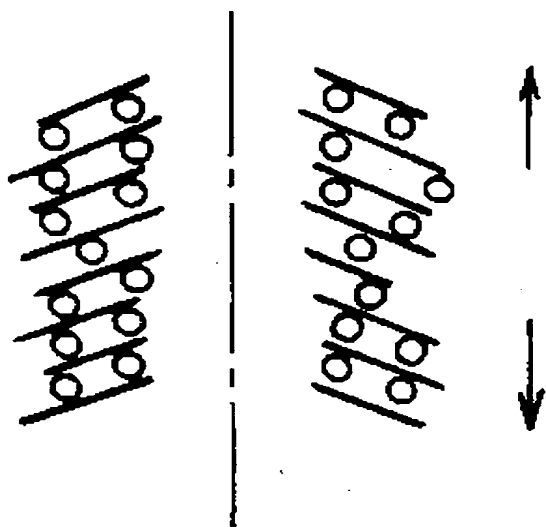


FIG. 11

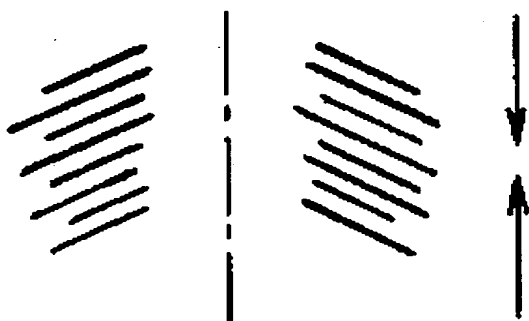
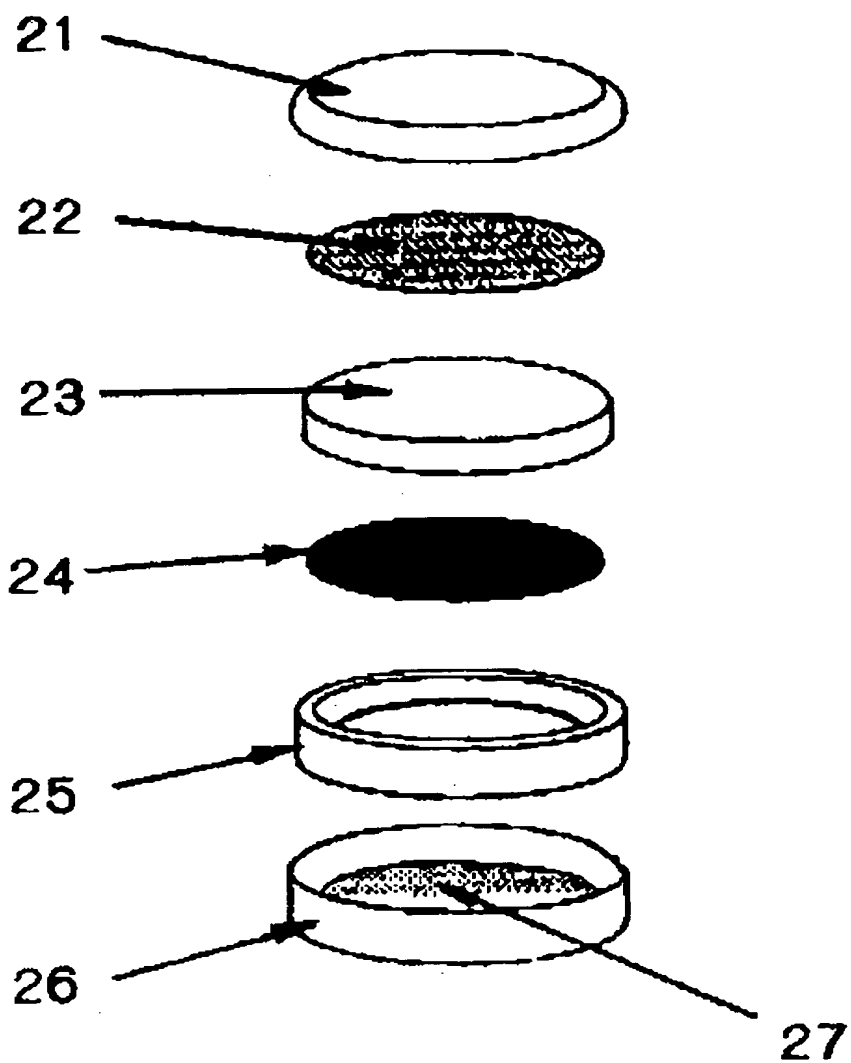
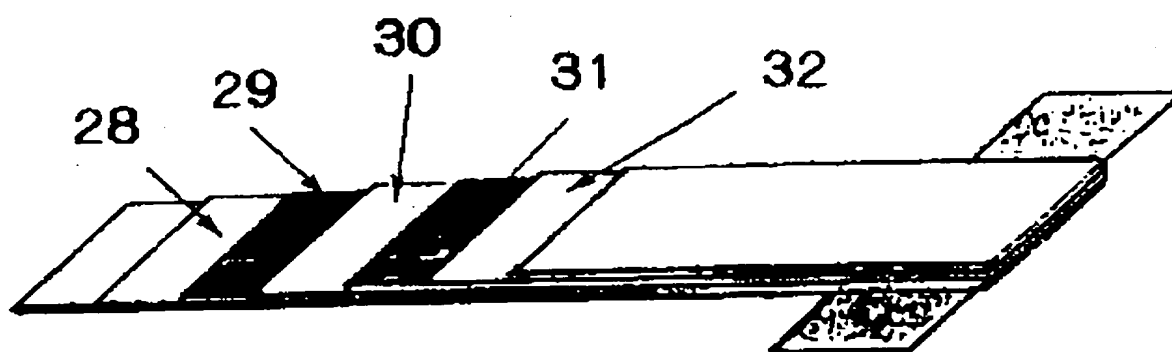


FIG. 12



**FIG. 13**



[DOCUMENT NAME] ABSTRACT

[ABSTRACT]

[OBJECT] To provide an electrode material which can provide an improved battery lifetime, an increased energy density for increasing the battery capacity and which is superior in electrical conductivity and electrode reinforcement.

[ARRANGEMENT] An electrode material for a lithium secondary battery according to the present invention is characterized by that it comprises a carbon fiber formed with vapor growth, the carbon fiber having a number of bottomless cup-shaped carbon mesh layers stacked together, and an area of a portion of the edges of the carbon mesh layers exposed on the exterior surface of the carbon fiber is equal to or larger than 2% of an area of the exterior surface of the carbon fiber.

[SELECTED FIGURE] FIG. 2